
AN INTEGRATED TREATMENT OF SIMPLE DISSOCIATION EQUILIBRIA IN SOLUTION¹

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ABSTRACT

A new and elementary synthesis for all simple dissociative equilibria of the form $AB \rightleftharpoons A + B$, where A and B are present in equal and very dilute concentrations can be developed by use of the Law of Mass Action. Solution of the non-dimensional quadratic equation, $R = K/C = X^2/C(C-X)$, for X, over a wide range of K-to-C ratios (preferably by computer), provides values of the degrees of ionization or hydrolysis applicable to all general processes of the schematic type presented above. For visual interpolative reference, a plot of $\log R$ versus $\log [P^2/(100-P)] - 2$ yields a straight line with a slope of unity. Agreement of readily obtainable laboratory data with these theoretical values serves as a ready check on the system under study for approach to "ideal" behaviour.

INTRODUCTION

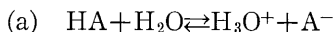
Most textbooks of beginning chemistry discuss the solution of problems in aqueous hydrolysis or ionization of weakly acidic and basic species adequately together under headings such as "acid-base equilibria." However, individual type examples are usually illustrated in these books without sufficiently emphasizing the completely general mathematical approach to which both of the above kinds of solution phenomena lend themselves.

THEORY

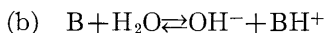
Consider the following four generalized and familiar cases of such processes

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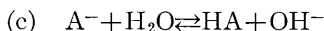
which are applicable both to monoprotic and monacidic acids and bases and to non-amphoteric anions and cations.



$$K = K_A$$



$$K = K_B$$



$$K = K_H = K_W/K_A$$



$$K = K_H = K_W/K_B$$

Equations (a) and (b), of course, represent the partial ionization in water of any weak acid or base, while the second pair of equations are stylized expressions for the hydrolyses of the conjugate anion of the acid or conjugate cation of the base here

K = a generalized equilibrium constant.

K_A = ionization equilibrium constant for the weak acid.

K_B = ionization equilibrium constant for the base.

K_H = hydrolysis equilibrium constant.

K_W = auto-ionization constant of water *under the conditions of measurement*.

It is essential to understand at this point that both the foregoing and the subsequent discussions are completely independent of factors such as temperature, type of equilibrium, or ionic strength (defined as $\mu = (\sum MZ^2)/2$, where M = molarity of ion Q and Z = charge of ion Q).

The nominal concentration of any of the above species can be defined as C and the equilibrium constant as K . Then, according to the Law of Mass Action,

$$K = \frac{X^2}{C-X} \quad (1)$$

where X = amount of ionization or hydrolysis in concentration units, generally moles per liter. The units of K , it should be noted, are the same as those of X . Solution of this expression for X by the exact algebraic "completion of the square" method to insure complete applicability (House and Reiter, 1968, discuss the comparative errors and the exact solution of hydrogen-ion calculations) gives $X = -K/2 + (K^2 + 4KC)^{1/2}/2$. By introducing a new parameter R , as equal to K/C , we obtain

$$R = K/C = \frac{X^2}{C(C-X)}, \quad (2)$$

a dimensionless equation.

If the degree of acid-base dissociation or hydrolysis is set as $D = X/C$, and the percent of the process $P = 100X/C$, equation (1) can be solved as follows for D in terms of any arbitrary value of R .

Since

$$K = RC$$

$$\text{then } D = \frac{X}{C} = \frac{(R^2C^2 + 4RC^2)^{1/2} - RC}{2C} \quad (3)$$

$$\text{and } D = \frac{(R^2 + 4R)^{1/2} - R}{2} \quad (4)$$

$$P = \frac{(R^2 + 4R)^{1/2} - R}{0.02} \quad (5)$$

In this way, a simple mathematical formulation for ionization or hydrolysis is obtained which depends *solely* on the ratio of K to C and is independent of any other variable. Values of D or P can be easily tabulated for any desired range of K/C; this is best done by a computer program. A 10- to 100-fold spread is convenient for ease in graphing, as shown in Figure 1.

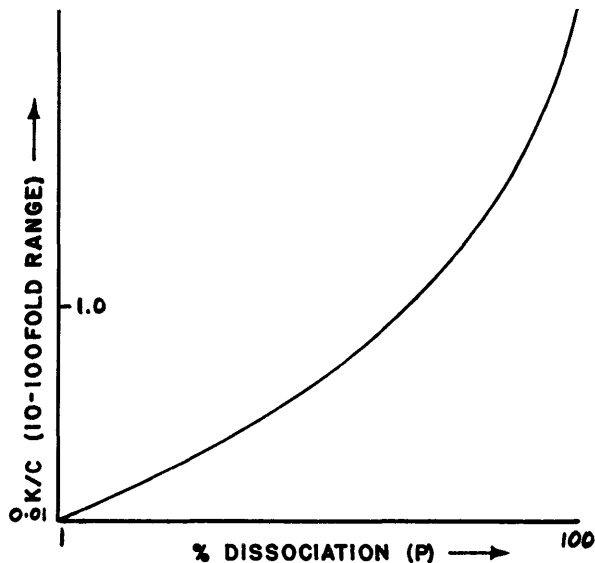


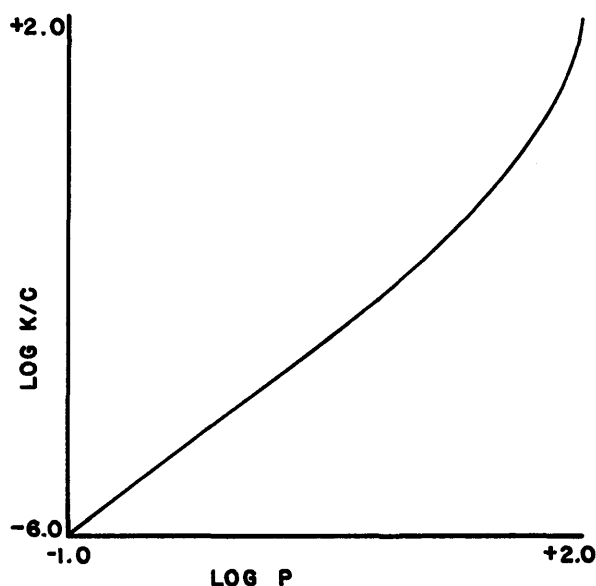
FIGURE 1. Plot of K/C or R vs. P.

For the solution of most practical examples encountered in a general chemistry course, it is advisable to work over a 10^8 K/C interval, that is, from $R = 100$ to $R = 10^{-6}$. For processes with $K = 10^{-2}$, this will include C values as low as 10^{-4} M. At the other extreme, if $K = 10^{-10}$, C may be as high as 10^{-4} M. R values lower than 10^{-6} and higher than 100 can be calculated, but with little added physical significance in terms of extent of equilibrium attainment as the data below indicate.

TABLE 1

R	P
10^{-6}	0.10
10^{-5}	0.32
10^{-4}	1.00
10^{-3}	3.11
10^{-2}	9.51
10^{-1}	27.02
1	61.80
10	91.61
100	99.02

These values can be plotted as follows. To compress the Y-axis, log K/C values are used as ordinates and, for a simpler graphical shape (to aid interpolation), log P (or D) as abscissas in Figure 2. Substituting CD for X in equation (2),

FIGURE 2. Plot of $\log P$ vs. $\log K/C$ or R .

$$R = \frac{C^2 D^2}{C(C-CD)} \quad (6)$$

$$R = D^2/(1-D) \quad (7)$$

Since $D = 0.01 \times P$, equation (7) may be rewritten as

$$R = \frac{P^2 \times 10^{-4}}{(1-0.01P)} \quad (8)$$

$$R = P^2/[100(100-P)] \quad (9)$$

For the latter identity,

$$\log R = \log [P^2/(100-P)] - 2 \quad (10)$$

$$\text{or} \quad \log R = 2 \log P - \log (100-P) - 2 \quad (11)$$

Figure 3 shows a log-log plot of equations (7) and (10).

A straight-line graph with a slope of unity passing through the origin is obtained for any concomitant range of R and P (or D) values. This plot serves as a very simple unambiguous check on the agreement of theoretical with experimental data.

SUGGESTIONS FOR EXPERIMENTS

Computer Programming

A program may be written which, for any arbitrary value of C , calculates D , P , $\log D$, $\log P$, R , $\log R$, or $\log [P^2/(100-P)] - 2$ over a suggested range of at least 10^8 . By suitable ordering of the output data, this is used as input for a series of graphs similar to Figures 1, 2, and 3; a plot of $\log R$ versus P (or D) is interesting because of its sigmoid appearance, but is not very practical as mentioned earlier.

LABORATORY WORK

The basic technique to be used has been described elsewhere (Bada, 1969) and may be employed to find the pH of acids, bases, or salts at various temperatures and ionic strengths where the K_A or K_B values are known (Weast, 1969, p. D-115-

120; Rieman *et al.*, 1951, p. 466–469). Listings of K_w at non-ambient temperatures are also available for hydrolysis computations (Clever, 1968). If desired, K may first be determined experimentally by pH measurement under a variety of conditions produced by variations in concentration, temperature, and ionic strength.

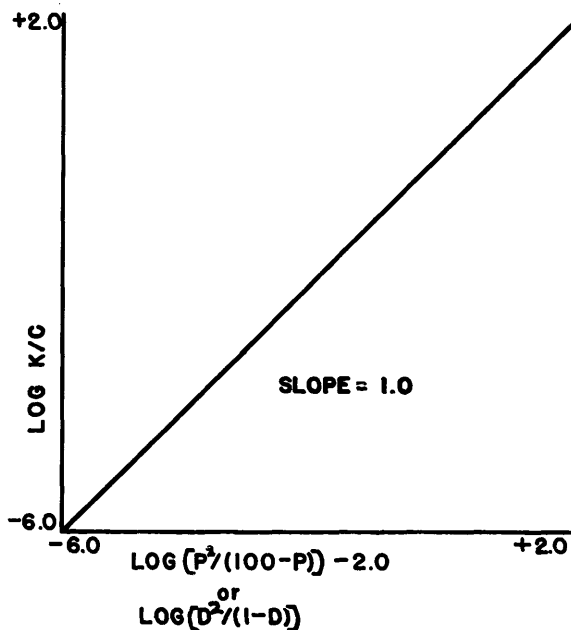


FIGURE 3. Plot of equations (7) and (10).

Using the pH values found, values of $[H_3O^+]$ for equations (a) and (d) as well as $[OH^-]$ for (b) and (c) can be established. These are equal to X , as in equation 1. Knowing X , values of P or D may readily be evaluated for the system under study and a graph such as Figure 3 drawn and compared with the theoretical plot. Experimental values for this graph may be fitted to the best straight line by a standard least-squares-fit technique (Klotz, 1964, p. 25). Using a computer program the experimenter may then offer reasonable explanations for any discrepancies in linear slope or aberration in his data points consistent with the equilibrium being considered. All programs referred to in the article may be obtained on request from the author.

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